

# Energy Transfer Processes in DNA-Organized, Multi-Segmental Chromophore Stacks

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**Abstract:** We are constructing and investigating DNA-based, multi-segmented chromophore systems. This will allow us to study energy transfer between chromophore over several intervening DNA bridges and to test the limits of the number of consecutive segments that still contribute to energy harvesting. The concept of interposed DNA base pairs should enable the construction of chromophore architectures in which distinct numbers of light-harvesters and acceptors are placed at well-defined positions - rather than distributed randomly - still profiting from a self-assembling synthesis route and, at the same time, maintaining DNA base pairing specificity.

## Introduction

In previous work we described and studied energy transfer processes in different types of DNA-assembled multi-chromophores (phenanthrenes and pyrenes).[1] Excitation of phenanthrene in these systems leads to highly efficient excitation energy transfer to pyrene (*non-segmented*, see Figure 1). Quantum yield measurements and transient absorption spectroscopy indicate that the energy is transferred over a delocalized excited state formed by  $\pi$ -stacked phenanthrenes (see Figure 1).[2] Ongoing studies show that energy transfer also takes place when the phenanthrene antenna is 'interrupted' by DNA base pairs (*segmented system*, see Figure 1). The energy transfer is remarkably insensitive to a small number (i.e. 1 or 2) intervening DNA base pairs. The efficiency of this 'DNA-tunnelling' drops off significantly only when the phenanthrene antenna is separated from the energy acceptor by at least three base pairs. Further supramolecular polymers are formed by phenanthrene/pyrene oligomers (without DNA).[3,4] Randomly distributed pyrenes lead to the formation of aggregates with light-harvesting properties (see Figure 2).

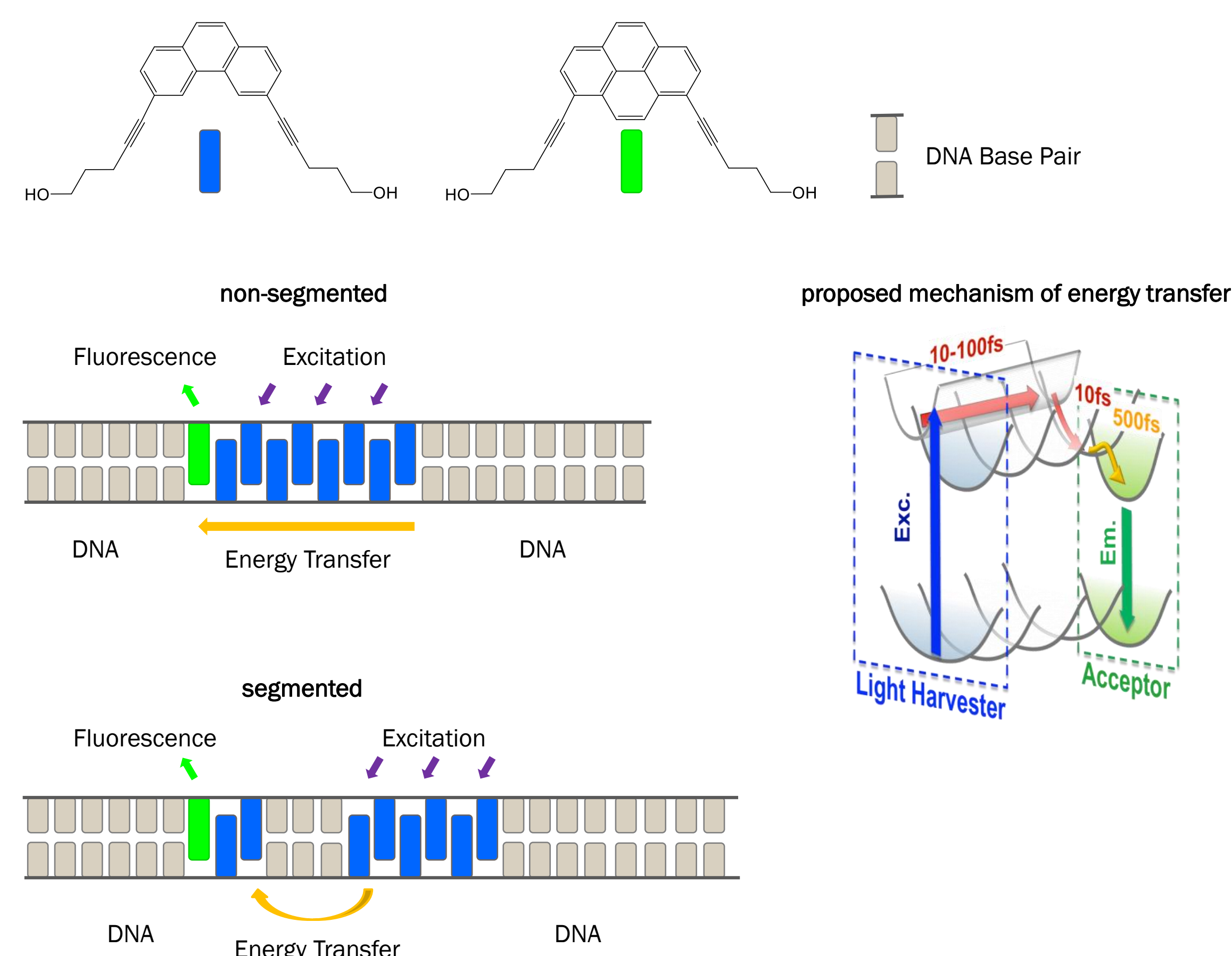


Figure 1. Non-segmented: a DNA duplex containing a stack of chromophores. Segmented: a DNA duplex containing a stack of chromophores separated by a given number of DNA base pairs.

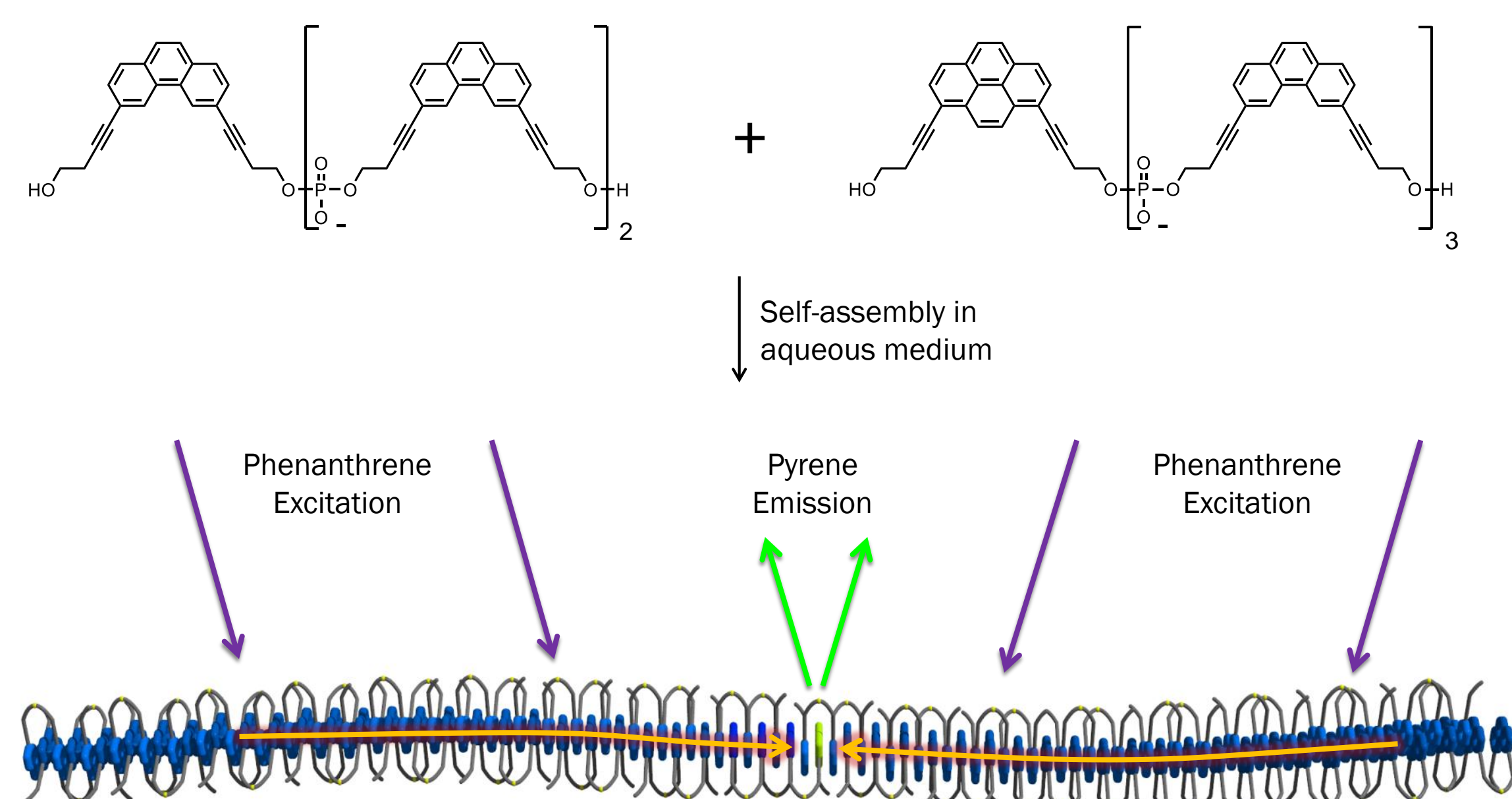


Figure 2. Light-harvesting supramolecular fibres formed by self assembly of phenanthrene and pyrene oligomers.

## Project (Phase III)

We plan to apply these findings to the design and construction of DNA-based, multi-segmented chromophore systems. This will allow to investigate energy transfer over several DNA bridges (*multi-segmented*, see Figure 3) and to test the limits of the number of consecutive segments that still contribute to energy harvesting. Development of such type of a light-harvesting antenna will also open ways of forming multi-chromophores in a selective manner (*multi-segmented and different chromophores*, see Figure 3). Eventually, the concept of intervening DNA base pairs should enable the construction of chromophore architectures in which distinct numbers of light-harvesters and acceptors are placed at well-defined positions but still profiting of a self-assembling synthesis route. This will be particularly helpful for the synthesis of supramolecular polymers (*multi-segmented polymer*, see Figure 3).

The design, synthesis and spectroscopic investigation of the described DNA-based architectures in close collaboration with our colleagues of the NCCR MUST network (Feurer, Cannizzo, Monari, Röthlisberger) would significantly advance our understanding of energy transfer processes in  $\pi$ -stacked multi-chromophores. It is planned, via ultrafast 1D and 2D DUV-to-Vis transient absorption measurements, to characterize the relevant time scales of the energy transfer processes, the involved excited states and their degree of delocalization, inter-chromophore couplings, the role of the DNA scaffold and of the solvent dynamics.

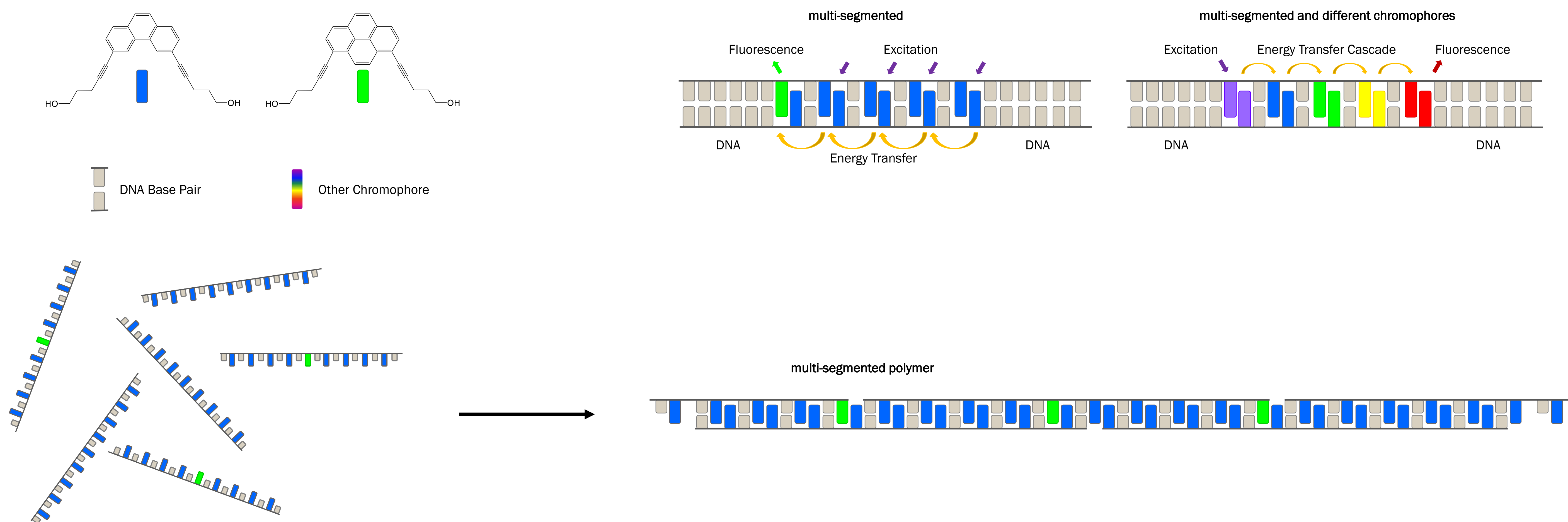


Figure 3. Illustration of DNA-organized multi-chromophoric architectures. Future studies will be aimed at the construction and investigation of multi-segmented and polymeric systems. Explanation of terms - multi-segmented: multiple pairs of chromophores that are always separated by at least one DNA base pair; different chromophores: chemically different types of chromophores available in our group; multi-segmented polymer: polymers of DNA and artificial building blocks that are formed via Watson-Crick specific base pairing by intervening nucleotides.

## References

- [1] F. Garo, R. Häner, *Angew. Chem. Int. Ed.*, 2012, 51, 916-919.
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- [4] C.B. Winiger, S. Li, G.R. Kumar, S.M. Langenegger, R. Häner, *Angew. Chem. Int. Ed.*, 2014, 53, 13603-13613.